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INSTRUMENT FOR DETERMINING THE DIRECTION OF DIP IN CORES TAKEN IN INCLINED HOLES.*

By C. F. C. Moore, A.R.S.M., and N. F. Brown.

Summary.

The determination of the direction of dip as shown in a core with respect to north can be made with fair accuracy—in all but vertical wells—by correlating the core with the direction of deviation of the well, which in turn can easily be determined by the single-shot type of inclinometer.

A simple method of correlation is to obtain an acid-etch in a glass bottle attached to the core with its long axis parallel to the core-barrel; the low-point of the etch will then indicate the direction in which the well is deviating. An instrument to obtain such an etch is described.

The core is obtained with a conventional core-barrel, preferably of the non-rotating type, in the normal manner. At a pre-determined time coring is stopped, and the instrument, which is run inside the core-barrel, attaches itself to the top of the core. After a short interval the core is burnt-in, pulled, and carefully extracted from the core-barrel.

By means of suitable circular protractors, the dip in the core is correlated with the low-point of the acid etch, and hence with true north by correlation with the single-shot inclinometer reading.

Early in 1939 a test-well coring continuously on the gentle flank of a small, sharply folded asymmetrical anticline in Burma suddenly encountered steep dips. It was thought that these steep dips might possibly be associated with faulting, or that they might indicate that the well had gone over the crest and was drilling in the steep limb of the fold. If the latter explanation were correct, it was clear that it would be useless to carry the well deeper. It was therefore essential that the direction of dip should be determined with the minimum of delay.

Efforts to obtain a Schlumberger Electro-magnetic Dip Meter revealed that all the instruments in the East were fully occupied, and that an instrument would have to be obtained from France, a matter of at least six weeks. An even longer interval would elapse before the results from a Polar Orientation of a core, carried out in America, would be available. The instrument here described was therefore designed and, successfully run several times in this test well, gave reproducible results, and provided the necessary information as to the direction of dip.

General Principles.

The use of the single-shot type of inclinometer makes it possible to obtain an accurate directional survey of a well as the drilling proceeds. Providing that a well was not absolutely vertical, it appeared that all that was required to determine the direction of dip in a core was to correlate the core with the direction of deviation of the hole at that particular point. The direction of deviation being known from the single-shot

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inclinometer reading, it would then be possible to determine the direction of dip in the core.

A simple method of attaining this correlation would be by the attachment of an ordinary acid bottle to the core after it had been taken, but before it had been broken off from the parent strata. The low-point of an ordinary hydrofluoric-acid etch on the acid bottle would then indicate the direction of deviation of the hole, which in turn could be interpreted in terms of true north from the single-shot inclinometer reading.

It was necessary to design an instrument which could be run inside the core barrel and which would only attach itself to the top of the core after the core had been cut; and to arrange matters so that immediately after the instrument had attached itself to a core, a clear acid etch on the glass acid bottle would be quickly made, without greatly disturbing the normal safe coring procedure. The instrument would then have to maintain its relation to the core undisturbed by subsequently burning-in the core and pulling-out the core barrel.

Method of Running.

The core barrel used with this instrument is preferably of the non rotating type, and in practice the instrument (which is about 45 inches long overall and weighs about 70 lb.) is run inside the core barrel attached to the upper valve assembly in the manner shown in the accompanying figure. The core barrel is run in in the normal manner, and a suitable length of core taken, say 8–10 feet in a 20-foot core barrel. The instrument is provided with a time release, which can be set to trip after a suitable interval which will allow time for running in and cutting the core. A little before the predetermined time, coring is stopped with the bit on bottom, circulation being maintained. On the instrument being released it falls down the core barrel, and the sharp spike, which is set eccentrically on the bottom of the instrument, penetrates the top of the core and fixes the instrument in relation to the core. It is desirable to arrange matters, as far as possible, so that the top of the core is fairly soft, preferably shale.

Should the core be lost, the instrument is retained in the core barrel by the core catcher.

Immediately after the instrument is fixed to the top of the core, an acid-bottle reading is taken, an etch being made by hydrofluoric acid in a suitable size of glass acid bottle the relation of which with respect to the eccentrically mounted spike is known. In order to preserve the etch when made, water is later added to the acid in the glass bottle, and not only dilutes the acid, but also raises its level. The time required for the complete operation of taking the acid-bottle reading is about 2½ minutes.

The core is then burnt in in the usual way and the drill-pipe pulled. The core is very carefully extracted from the barrel (the upper end of which is kept slightly raised), in order not to disturb the relation between the instrument and the top of the core. It has been found useful to cut a line up the side of the core as it is extracted, in order that the entire length of core may be correlated with the instrument, in case the core breaks while being extracted, or it is subsequently found that there are

no suitable indications of the dip in the upper part of the core near the instrument. After pulling the core, a single-shot inclinometer reading is taken to give the direction of deviation of that part of the hole from which core has been cut.

Using suitable circular protractors to fit round the core and the acid bottle, it is possible to correlate the direction of dip in the core with the orientation of the instrument, and so with the low-point of the etch of the contained acid bottle; thus the dip is correlated with the direction of deviation, which is known in relation to north from the inclinometer reading.

Determinations of the direction of dip are normally accurate to within plus or minus 10°, but the accuracy depends on the steepness of the dip as shown in the core and on the angle of deviation of the well. The greater both these factors, other things being equal, the greater the accuracy of the determination.

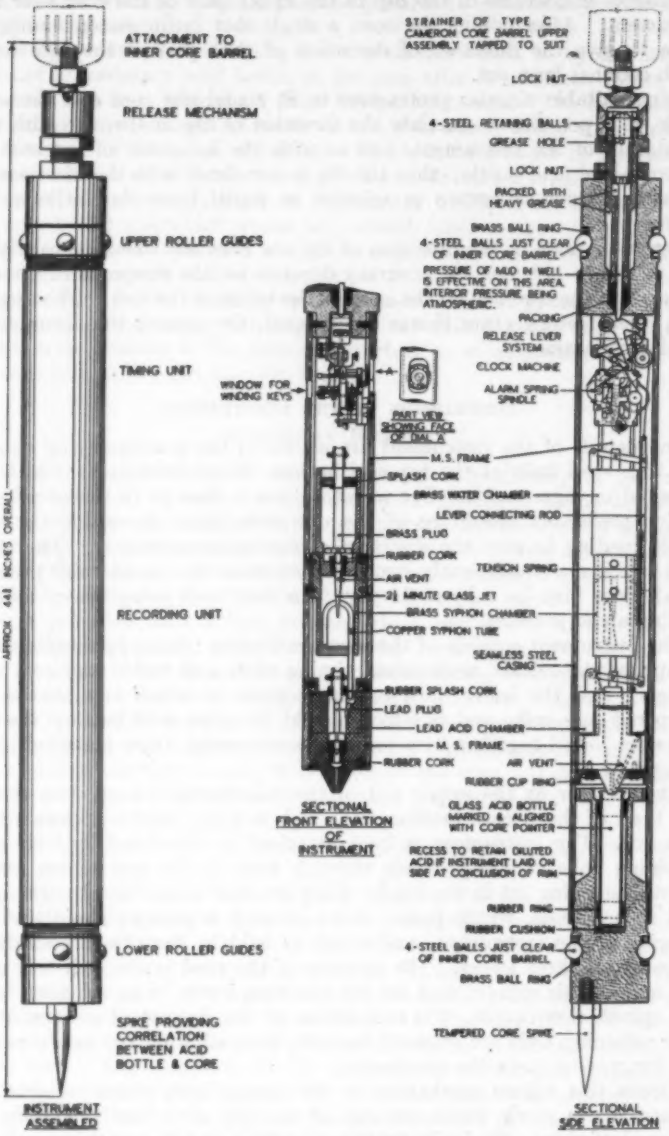
Description of the Instrument.

The details of the instrument are shown in the accompanying figures. The four steel balls at the top and bottom of the instrument, which are mounted in cages and are free to rotate, are a close fit in the core-barrel (which preferably should be of the one-piece type), to enable the acid-bottle reading to give the direction of deviation accurately. The outer steel case is made sufficiently strong to withstand the considerable pressure to which it may be subjected—say, in a deep well using heavy mud or drilling under pressure.

The instrument consists of three separate parts: the upper unit, which comprises the release mechanism, timing unit, and water and acid containers; and the lower unit, on the bottom of which is mounted the tempered core spike and in which is held the glass acid bottle; the two units are joined together by a seamless steel casing, taper threaded joints being used.

The strainer at the upper end of the core-barrel is tapped to receive the head of the release mechanism, which is firmly held in position by a lock-nut. The instrument is held attached to this head by four steel retaining balls, which protrude through holes in the top of the instrument into a ring cut in the head. They are held in position by the upper end of a spindle, which passes down through a packing-gland into the interior of the instrument, and which is held in the raised position by a system of three levers. The pressure of the mud in the well acts upon the area of this spindle, and, on the retaining levers being released, forces the spindle downwards. On completion of this downward movement the four retaining balls are released inwards, thus allowing the instrument to fall by gravity down the core-barrel.

Below this release mechanism is the timing unit, which consists of a robust alarm clock which can be set to trip after any predetermined interval of time. To facilitate this, the clock is fitted with a small dial (Dial A) in place of the usual dial on the clock-face by which the alarm clock is set. The clock rotates this dial (which is divided into 12 hours by quarters) one revolution in 12 hours, and the required time interval is



INSTRUMENT TO DETERMINE DIRECTION OF DIP IN CORES

FIG. 1.

set directly by rotating the small hand on the dial until it indicates the required interval.

On the clock alarm mechanism being tripped, the alarm-spring spindle rotates and winds up the flexible thin wire cable attached to it. This cable pulls down the first of a system of three levers. The first lever is normally kept in place by a light spiral spring. This first lever in turn releases the second lever, which is under tension from a fairly strong spiral spring anchored to the frame just above the lead acid chamber. This second lever in turn releases the third lever, which is of robust construction, and is designed to retain the spindle in the upper position against the well pressure and, on release, to utilise the well pressure acting on the spindle to operate the acid-bottle mechanism. In this way the effort of the clock is limited to the release of the first lever, a task easily within its capabilities.

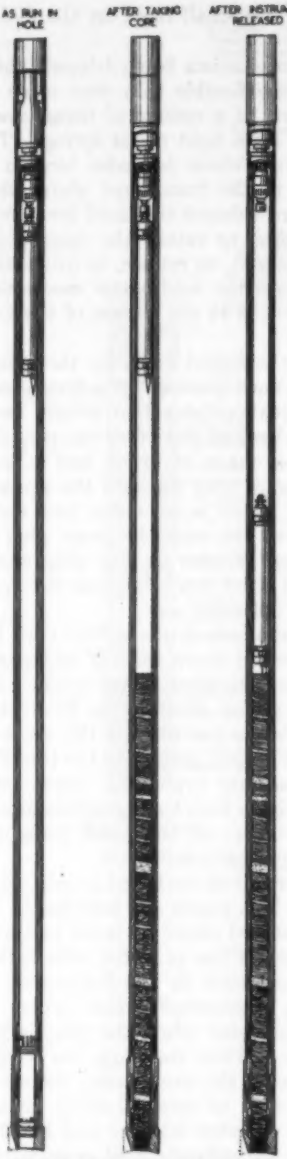
When the third lever is forced down by the spindle, a thin wire cable attached to its lower branch passes over a deep-grooved pulley and raises the connecting-rod which operates two levers, one of which raises the plug in the water chamber and the other the plug in the acid-chamber.

The water chamber is made of brass, and is mounted above a brass syphon chamber. A brass plug fits into the upper part of the hole cut through a rubber cork which is cemented into the bottom of the water chamber. A little above the cork the brass plug is fitted with a guide in the shape of a cross. Higher on the plug spindle, above the water level, a cork is mounted which is a loose fit in the upper end of the chamber and prevents the water splashing out.

In the lower end of the hole in the rubber cork is mounted a glass jet, the end of which is ground down until it will pass the required volume of water from the water chamber to the syphon chamber in exactly 2½ minutes. The brass syphon chamber is fitted with a copper syphon tube, which, after the water has reached the necessary level, syphons the water down through the special opening in the top of the lead-acid chamber. To ensure that the necessary syphoning action takes place even though some of the water may have been lost by splash or evaporation, the syphon tube is set to syphon before all the water from the upper chamber has passed down into the syphon chamber.

The acid chamber is made of lead, and is only required to hold sufficient acid to fill up about 1 inch inside the acid-bottle. The plug in this case is made of lead, and is fitted above its lower end with a guide in the form of a cross. The bottom of the plug fits into the hole in a rubber cork, which is cemented in position in the bottom of the chamber. At the upper end of the plug is mounted a thin rubber cork, which is a tight fit in the top of the chamber when the plug is in its lowered position, thus preventing splash. When the plugs are withdrawn from the water and the acid chambers at the same time, the acid flows down into the glass acid-bottle, and after an interval of 2½ minutes the water syphons down through the acid chamber into the acid bottle.

The strength of the hydrofluoric acid is so adjusted that it will make a good clear etch at the well temperature in 2½ minutes on the type of glass acid bottle to be used. On the conclusion of this period it is diluted with water.



METHOD OF RUNNING INSTRUMENT IN CORE BARREL

FIG. 2.

Below the lead acid chamber is mounted a rubber cup-ring, which prevents the acid from running up and damaging the clock when the core-barrel is laid on its side at the conclusion of the run.

The tapered core-spike is set eccentrically on the bottom of the lower unit which carries the acid-bottle, and a line is scribed on the top of this unit indicating the direction of the spike from the centre. The acid-bottle, which is made of clear glass and is $1\frac{3}{32}$ inch O.D. and $6\frac{1}{4}$ inches long, sits on a rubber cushion, and is fitted with two rubber rings, which not only preserve the bottle from damage, but also ensure that it is concentric with the axis of the instrument. A vertical line is scribed on the acid bottle with a stellite pencil, and this line is made to coincide with the line showing the direction of the spike: thus providing the required correlation between the mark made by the spike on the top of the core and the direction of deviation shown by the acid-bottle.

A recess is cut in the lower unit of sufficient capacity to take the liquid contents to the acid-bottle when the instrument is laid on its side. As will be seen from the drawing, provision is made for equalizing the pressures within the various units of the instrument.

This instrument was designed for the Indo-Burma Petroleum Company, Ltd., to whom the authors tender their thanks for permission to publish this description.

A PRELIMINARY STUDY OF THE CHEMICAL CONSTITUTION OF KEROGEN.*

By A. L. Down, Ph.D., A.R.C.S., D.I.C., and G. W. Himus, Ph.D., M.I.Chem.E., A.R.C.S.

Although the existence of rocks which yield oil on heat treatment has been known for several centuries, and although shale-oil industries have been in operation for more than a hundred years, even to-day very little is known of the organic matter or "kerogen" from which these oils are derived. The voluminous literature dealing with the oil-shales and shale-oils is concerned mainly with the economic and technical problems of obtaining and refining the crude oils; the chemistry of the shale-oils, particularly the lighter fractions, has been studied in some detail, but there has been little or no attempt at a fundamental attack on the chemical constitution of the parent kerogen. It should here be emphasized that the term "kerogen" does not imply any particular compound or group of compounds, but is merely a convenient name for the organic matter from which oil is obtained when rocks containing it are heated; hence the kerogens of different deposits may be chemically different, and may even vary in different parts of the same seam.[1]

The study of the chemistry of kerogen follows the same general lines as the study of coal, and involves two main series of operations—namely, (*a*) the determination of the chemical composition, and (*b*) investigation of the chemical constitution. With regard to the chemical analysis, whereas, with coals, determination of the chemical composition is straightforward, since the content of inorganic matter is generally low, in dealing with most kerogen rocks the (generally) high content of mineral matter introduces serious complications, and it has recently been shown by one of us (A. L. D.)[2] that unless the sample has been substantially completely de-ashed, the results obtained for the composition of kerogen are quite unreliable. Thus, many analyses of coals of all ranks are available from which it has been possible graphically to prove the continuity of composition of members of the peat-to-anthracite series, and to link the compositions of the less mature members of the series with those of modern plant materials, as has been done by O. C. Ralston,[3] G. Hickling,[4] and others. On account, however, of the difficulty of isolating the kerogens, the true compositions of only a few samples are known, and although these indicate that they do not form a section of the peat-to-anthracite series, by reason of their higher contents of hydrogen, it will be necessary to accumulate analytical data on several hundred samples before any conclusions can be reached with certainty as to the existence of similar "maturing curves" for kerogen rocks.

The problem of the elucidation of the chemical constitution of kerogen may be attacked in three main ways: (*a*) by studying the mechanism and

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course of its thermal decomposition, with examination of the products, (*b*) investigation of the action of reagents, and (*c*) by studying the products of controlled oxidation.

The thermal decomposition of the organic matter is of outstanding importance, since the industrial application of the kerogen rocks depends on it. The actions whereby oil and gas are derived have been studied by a number of workers, usually under conditions which are less drastic than those employed in retorting. C. Engler [5] found that when a sample of New South Wales algal shale was heated for 5 hours to 400° C., the amount of material soluble in benzene increased from 1·4 to 55·2 per cent., which indicated that the initial stage in the decomposition was the formation of a soluble bitumen. R. H. McKee and E. E. Lyder [6] isolated an intermediate compound from Parachute Creek kerogen shale by vacuum distillation, and found it to be highly unsaturated, as shown by its almost complete solubility in concentrated sulphuric acid; the material was a solid or semi-solid bitumen which, on further heat treatment, broke down into an oil which was only about 50 per cent. unsaturated. From similar work, C. O. Blackburn [7] came to the conclusion "that the oil-forming constituents in Elko, Nevada, shale kerogen are products of polymerized montan wax, which upon thermal decomposition, de-polymerizes, and forms first, a primary product, montan wax." A. J. Carlson [8] examined the effect of heat treatment *in vacuo*, at 250°, 300°, and 350° C., on the solubility in carbon tetrachloride of the organic matter of three shales, derived respectively from Grand Valley (Colorado), Soldier Summit (Utah), and Montgomery County (Kentucky). The samples contained about 90 per cent. kerogen, the greater part of the mineral matter having been removed by treatment with acids. The gases evolved contained carbon dioxide, from which Carlson concluded, in view of the fact that the samples were heated in the absence of air and the low temperatures employed, that carboxyl groups were present in the kerogen. Work on samples from which varying amounts of mineral matter had been removed led to the conclusion that there was some chemical combination ("either adsorbed or true compound") between the organic and inorganic constituents. Recent work at the Imperial College [9] has shown that after removal of the mineral matter from a kerogen rock the solubility of the kerogen in acetone and chloroform may be materially increased, and examination of the absorption of shale-oil by clays has suggested that there is physical adsorption of part of the "soluble" material.

The study of the chemistry of kerogen would be simplified if all or a considerable part of the kerogen were soluble in organic solvents, but numerous investigations have shown that the insolubility of kerogen in organic solvents is a characteristic property which serves to distinguish true kerogen rocks from such materials as oil- or tar-sands, bituminous limestones, etc.

That certain kerogens, such as those in the shales of De Beque (Colorado) and Ione (California), are unsaturated is shown by their vigorous action with chlorine; R. H. McKee [10] found that absorption of chlorine caused a considerable increase in the solubility of the kerogen in alcohol.

Examination of the oils from different shales has proved that the kerogens were chemically very different. Whereas the Scottish shale-

oils, and also those from Elko (Nevada), Capertree, and Newnes (New South Wales), contained considerable proportions of paraffin wax (about 12 per cent.), and generally resembled the paraffin-base crudes, oils from Swedish and Kentucky shales were asphaltic, paraffin wax being absent, while the oils from the shales of the Green River formation (Parachute Creek, Colorado, Soldier Summit, Utah, etc.) resembled mixed-base petroleums. The lighter fractions of certain shale-oils have been studied in some detail; Scottish [11] samples have been shown to consist almost entirely of paraffins, naphthenes, and olefines, and although aromatic hydrocarbons have been reported, the general opinion is that, if present at all, it is only in very small amounts. J. M. Petrie [12] found that the oil from the Joadja Creek algal coal (New South Wales) contained 9 per cent. of paraffin wax; the light fractions consisted of olefines and paraffins, the former preponderating. As the boiling point of the fractions increased, the percentage of olefines decreased, and none was detected in the fraction boiling above 280° C. The absence of aromatics in the oils does not imply that kerogen is entirely non-benzenoid in structure. Jones and Wheeler [13] and Pictet and Bouvier [14] have shown that the oils obtained by the distillation of bituminous coals *in vacuo* at 550° C. consist almost entirely of naphthenes and unsaturated hydrocarbons, notwithstanding the fact that on oxidation with alkaline permanganate, from 39 to 46 per cent. of the carbon of coal is converted into benzenoid acids. On the other hand, the presence of benzene, toluene, and *m*-xylene has been definitely established in Swedish shale-oils by Hellsing [15] and Holmberg.[16]

J. B. Robertson [17] oxidized samples of "oil shale, torbanite, cannel coal, peat, and lycopodium" with concentrated nitric acid. The products contained oxalic acid and other organic acids which gave empirical formulæ $C_{16}H_{22}NO_6$ and $C_{16}H_{24}NO_5$ when derived from Broxburn Main oil-shale and torbanite, respectively. He concluded that all the samples examined were of a similar nature, and arranged them in a series: lycopodium, torbanite, Broxburn oil-shale, peat, cannel coal, and bituminous coal, and suggested that each represented the end-point of decomposition of organic matter under a different set of conditions, thus directing attention to the profound importance of environmental influences in determining the final product obtained from a given raw material.

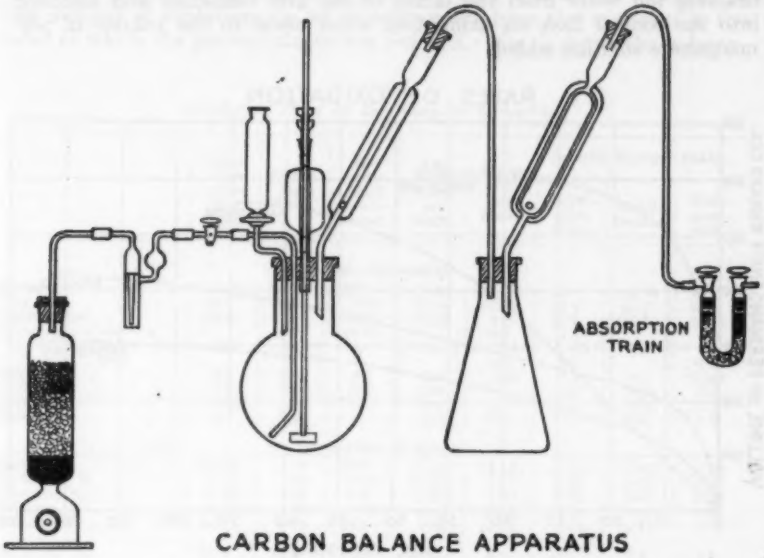
P. N. Kogerman [18] reported to the Glasgow Conference the results obtained by the mild oxidation of a rich sample of Estonian kukersite (algal limestone) with alkaline potassium permanganate at 30° C. About 8 per cent. of the kerogen was not converted into soluble products; the carbon balance was:—

Percentage of the carbon appearing in the products as:	
CO_2	35·6
Oxalic acid	43·8
Acetic and other fatty acids (mono- and di-basic)	21·6

One of the most important features of the results was the absence of any detectable benzenoid acids in the products, although benzenoid acids have invariably been important products of the oxidation of members of the peat-to-anthracite series.

The Present Investigation.

The most hopeful method for the preliminary study of the chemical constitution of kerogen was considered to be by controlled oxidation by alkaline potassium permanganate, and, with slight modification, the technique so successfully employed on coal by the late Professor W. A. Bone and his colleagues [19] was adopted. Oxidations may be carried out under "carbon-balance" or "bulk-oxidation" conditions, according as it is desired either to determine quantitatively the distribution of carbon among the various products of oxidation, or to prepare sufficiently large quantities of the soluble products for separation and identification.



CARBON BALANCE APPARATUS

Fig. 1.

Carbon-balance Oxidation.—The apparatus used is illustrated in Fig. 1. It consisted of a 2-litre bolt-head flask fitted with a motor-driven stirrer, tap-funnel, and condenser. From the condenser a tube led into a conical flask of some 750 ml. capacity, also fitted with a condenser, which was connected to an absorption train of calcium chloride and Sofnolite tubes. An amount of finely ground (100 mesh, I.M.M.) kerogen rock, equivalent to 1 gm. of carbon, was weighed into the flask and 100 ml. of 1·6 per cent. potassium hydroxide solution were added. The apparatus was swept out with air freed from carbon dioxide by being passed through a tower containing Sofnolite and a bubbler containing strong potash solution. Since, notwithstanding the alkalinity of the solution in the flask, a small quantity of carbon dioxide escaped during the oxidation, a weighed absorption train was attached to the second condenser, and a slow, continuous stream of CO_2-free air was passed through the system during the oxidation. The

reaction flask was heated by being immersed in a bath of glycerine, maintained by means of a thermostat at 115° C., so that the alkaline solution boiled gently and the shale was kept in suspension by the joint actions of the stirrer and the boiling of the solution. When the solution started to boil, potassium permanganate was added as a 3 per cent. solution from the tap-funnel, the addition being made at a rate equal to that at which the permanganate was being reduced; from time to time a sample of the solution was drawn up into the tube, the solid matter was allowed to settle, and the colour was observed. If the sample of solution was colourless, further permanganate solution was run in. During the oxidation the original volume of the solution was periodically restored by draining the water from the jacket of the first condenser and distilling into the conical flask an amount of water equal to the volume of permanganate solution added.

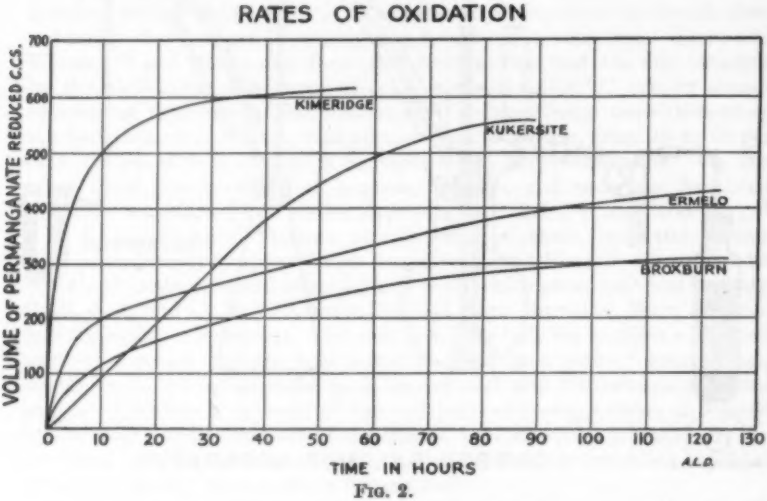


FIG. 2.

The rate of oxidation gradually decreased until it approximated to the rate of auto-decomposition of the permanganate (which had previously been determined under the conditions of the experiment); oxidation was then considered to be complete. Any carbon dioxide liberated during the reaction and remaining in the system was then swept into the absorption train, which was detached and weighed. The oxides of manganese and the residue from the shale were separated from the solution by sucking the latter off through a Jena-glass immersion filter, thoroughly washed with boiled-out distilled water, and the filtrate and washings were made up to 1 litre. The solids were then suspended in water, the oxides of manganese dissolved by means of sulphur dioxide, the residue was filtered off, washed, and dried, and the amount of unoxidised carbon determined by combustion.

The percentages of the original carbon oxidized to carbon dioxide,

steam-volatile acids, oxalic acid, and non-volatile acids were estimated as follows. The carbon dioxide was determined by acidifying 100 ml. of the solution with dilute sulphuric acid and sweeping the CO_2 into a weighed absorption train; the resulting acid solution was steam-distilled to obtain the steam-volatile acids, which were titrated by standard alkali and calculated to acetic acid. Oxalic acid was estimated by precipitation as calcium oxalate and subsequent titration with $N/10$ potassium permanganate. The non-volatile acids were determined by neutralizing 100 ml. of solution, evaporating to dryness on a steam-bath, the carbon in the residue being determined by combustion. These acids were partly benzenoid and partly straight-chain.

The very marked differences in the behaviour of different kerogens to this method of oxidation was at once apparent from the variation in the rates at which the permanganate was reduced. Fig. 2 shows the volume–

TABLE I.

Analytical Data on the Samples Examined.

	Kimeridge Kerogen Shale.	Ermelo Algal Shale.	Estonian Algal Limestone.	Amherst Kerogen Shale.	Kohat Kerogen Shale.	Scottish Kerogen Shales.		
						Broxburn Main.	Middle Dunnet.	Pumpherston.
Proximate Composition.								
Kerogen	59·25	53·65	52·0	53·05	11·85	26·0	16·25	18·2
Clay	16·6	31·3	9·25	24·55	41·95	43·6	45·8	45·5
Excess silica	12·35	11·3	5·75	12·65	8·0	10·7	20·7	19·75
Carbonates of calcium	1·35	0·5	26·95	0·1	20·3	1·9	6·8	4·9
,, magnesium			—		7·35	1·95		3·5
,, iron			—		3·3	9·7		1·9
Gypsum	3·5	0·1	0·5	0·9	0·45	0·3	0·1	Trace
Pyrite	1·9	0·95	2·0	0·9	—	1·3	0·5	2·0
Ferric oxide	2·35	—	—	2·6	—	—	6·05	2·2
Balance	2·7	2·2	—	3·55	6·8	—	3·8	2·2
Composition of Kerogen.								
Carbon, %	68·98	79·75	77·3	77·46	72·58	80·41	78·63	80·02
Hydrogen, %	7·10	7·82	8·65	11·08	8·11	8·67	8·17	7·65
Nitrogen, %	1·38	1·56	0·2	1·24	1·34	2·32	2·65	2·30
Sulphur, %	8·83	1·22	1·45	0·80	0·81	0·10	1·23	0·61
Oxygen (diff.), %	13·71	9·65	12·4	9·42	17·16	8·58	9·32	9·42
Oil yield,* %	25·5	16·8	—	34·3	4·9	13·6	7·9	8·6
	From the richest of the four seams near Kimeridge, Upper Jurassic.	From a bore-hole core, Moolfontein No. 287. Supplied by Dr. P. E. Hall of the Fuel Research Institute, Pretoria. Permo-Carboniferous.	Weathered sample from an outcrop at Kohtla. Ordovician.	Collected by Dr. Colter from 1 mile due east of Forest Post 63, Hitchens sheet, Amherst, Burma. Middle Tertiary.	Collected by Dr. Coulson from an outcrop near Kharak (Kark), N.W.F.P., India. Considered to be Lower Tertiary, probably Eocene.	Hopetown. Rich sample from Lodgment Dook, Eastside, Main Haulage Road. Seam 5 ft. 6 ins. thick, 504 ft. below surface.	Westwood Pit. South side of West Main Incline. Seam 9 ft. thick, 820 ft. below surface.	No. 3 Mine, Duddington. From Plain Shale Seam, No. 23 Level, No. 9 Dook. Seam 5 ft. 1 in. thick, 195 ft. below surface. Samples supplied by Scottish Oils, Ltd.

* Gray–King Assay.

time curves for a number of samples. Broadly, it was found that the slower the initial rate of oxidation, the smaller was the percentage of carbon converted to soluble products.

The general analytical data for the eight samples of kerogen rocks which have been examined by the "carbon-balance" method of oxidation are given in Table I, and the results are shown in Tables II to IV.

Kimeridge Kerogen Shale, Dorset (Table II).—This was the first shale to be examined; four carbon balances were obtained, the first before the modification of the apparatus for maintaining the concentration of the solution constant was introduced. The spent permanganate solution therefore diluted the liquor, resulting in less drastic conditions than obtained in subsequent experiments; this was equivalent to a shorter

TABLE II.

Carbon Balances on Kimeridge Kerogen Shale.

	1.	2.	3.	4.
		"Standard" conditions.		Kerogen at 3·3% mineral matter.
Percentage carbon as:				
Carbonic anhydride . .	47·97	49·76	47·78	51·20
Acetic acid . . .	3·10	8·32	9·57	8·52
Oxalic acid . . .	24·24	30·95	30·58	24·88
Non-volatile, non-oxalic acids	19·73	10·53	9·37	13·62
Total C in products . .	95·04	99·56	97·38	98·22
Unoxidized . . .	4·45	0·64	1·45	0·84
Total . . .	99·49	100·20	98·83	99·06
Distribution of Oxidized Carbon.				
Carbonic anhydride . .	50·5	50·0	49·0	52·1
Acetic acid . . .	3·2	8·4	10·0	8·7
Oxalic acid . . .	25·5	31·1	31·4	25·3
Non-volatile, non-oxalic acids	20·8	10·5	9·6	13·9
Total . . .	100·0	100·0	100·0	100·0
Oxidation time, hrs. . .	54	57	58	30
Ratio $KMnO_4/C$ . . .	17·1	18·4	19·0	19·0

time of oxidation. Two balances were carried out under the standard conditions, and the results serve to show the reproducibility of the results. Practically complete oxidation was secured, but in achieving this a portion of the higher acids formed in the earlier stages of the oxidation were further oxidized to carbon dioxide and oxalic acid. In researches on the permanganate oxidation of coals,[19] it has been shown that with the occasional exception of small quantities of succinic acid, the non-volatile acids were entirely benzene-carboxylic acids, and that the percentage of these acids and the other oxidation products steadily increased as the carbon was progressively attacked. Further, work on the permanganate oxidation of chemically pure acids [20] has shown that whereas benzene-carboxylic acids were not attacked, straight-chain acids were oxidized

fairly readily to carbon dioxide and oxalic acid. It must therefore be concluded that a considerable proportion of the non-volatile, non-oxalic acids formed in the initial oxidation of the Kimeridge kerogen shale are of a type not produced from coals, and the percentage of carbon oxidized to benzenoid acids cannot exceed 10.

A sample of Kimeridge kerogen (the mineral content of which had been reduced to 3·32 per cent.) was oxidized, and the rate of reaction was found to be nearly double that of the untreated samples. In 30 hours over 99 per cent. of the carbon was converted into soluble products; the solution was found to contain an appreciably higher percentage of non-volatile, non-oxalic acids. This presumably is explicable by the shorter time of oxidation having been insufficient for the further oxidation of all the straight-chain acids which were first formed.

Since the percentage of sulphur in Kimeridge kerogen is very high (8·83), the solution from the carbon balance oxidation was examined for sulphur compounds, and it was found that the whole of the organic sulphur had been oxidized to SO_3.

Ermelo Algal Shale, South Africa (Table III).—This material is entirely different, both in general appearance and microscopic structure, from the Kimeridge kerogen shale. Unlike the Kimeridge, the rate of oxidation

TABLE III.

Carbon Balances on Ermelo Algal Shale.

	1.	2.	3.		Total.
			i.	ii.	
			Stage oxidation.		
Percentage carbon as:					
Carbonic anhydride	19·48	30·68	25·72	11·36	37·08
Acetic acid	6·12	5·12	3·57	3·18	6·75
Oxalic acid	0·77	13·24	9·19	2·97	12·16
Non-volatile, non-oxalic acids	28·81	17·19	21·38	2·15	23·55
Total C in products	55·18	66·23	59·86	19·66	79·52
Unoxidized carbon	44·82*	34·19	40·14*	20·77	20·77
Total	100·00	100·42	—	—	100·29
Distribution of Oxidized Carbon.					
Carbonic anhydride	35·2	46·3	43·0	57·8	46·6
Acetic acid	11·1	7·7	6·0	16·2	8·5
Oxalic acid	1·4	20·0	15·3	15·1	15·3
Non-volatile, non-oxalic acids	52·2	26·0	37·7	10·9	29·9
Total	100·0	100·0	100·0	100·0	100·0
Oxidation time, hrs.	32	145	50	75	125
Ratio $KMnO_4$/C	7·1	13·2	—	—	12·1

* Unoxidized carbon obtained by difference.

was very slow, and although at the end of 32 hours the rate of reduction of permanganate was about equal to its rate of auto-decomposition, analyses showed that not more than 50 per cent. of the carbon had been

converted into soluble products. The most interesting feature of this balance is the very small percentage of carbon appearing as oxalic acid, whilst at the same time the total amount of non-volatile acids was very high, over 50 per cent. of the oxidized carbon being thus accounted for. In the second oxidation the run was continued until the amount of permanganate reduced was equal to that required for complete oxidation, as calculated from the first experiment; the total time was 145 hours. Examination of the resulting solution, however, showed that the percentage of carbon converted into soluble products had risen from 55 to only 66. The additional permanganate had therefore been largely employed in the further oxidation of non-volatile, non-oxalic acids formed in the earlier stages of the reaction to carbon dioxide and oxalic acid. The proportion of acids thus attacked is readily seen from the distribution of carbon in the oxidation products; the distribution of oxidized carbon is very similar to that obtained from the oxidation of immature coals such as brown coals and lignites. The percentage of carbon as non-volatile, non-oxalic acids—namely, 17, or 26 per cent. of the oxidized carbon—is much higher than that obtained from the Kimeridge shale. In view of the very long time of oxidation, and the very slow rate of reduction of permanganate during the final 20 hours, it may be concluded that these acids were benzenoid, since the aliphatic acids oxidize fairly rapidly.

In an attempt to obtain more complete oxidation, a sample of the algal shale was oxidized in two stages; after 50 hours the solution was sucked off via a Jena-glass immersion filter, a fresh volume of potassium hydroxide solution was added, and the oxidation was continued for a further 75 hours. The two solutions were worked up separately, with the results shown in columns 3 (i) and 3 (ii) of Table III; the former may be considered as an ordinary carbon balance intermediate between Nos. 1 and 2. This stage-oxidation was successful in reducing the amount of carbon in the residue to 20 per cent., the reduction of permanganate by preferential attack of the primary oxidation products having been prevented. Oxidation in the second stage proceeded very slowly, the kerogen residue being more resistant to attack than bituminous coals or anthracites; examination of the distribution of the 20 per cent. carbon oxidized in the second stage indicates that only a small part of the structure could be benzenoid.

Table IV summarizes the results of carbon balance oxidations of three widely differing types of kerogen rocks; each was much more resistant to oxidation than Kimeridge kerogen shale, and in no case was oxidation complete. A striking feature of the carbon balance on the Amherst shale is that, apart from carbon dioxide, only 7 per cent. of the carbon was oxidized to acids other than oxalic. The Amherst kerogen is distinguished by containing a higher percentage of hydrogen than any other kerogen examined, and is therefore more highly saturated. Similarly, nearly all the oxidized carbon of the Estonian algal limestone (kukersite) appeared either as carbon dioxide or as oxalic acid, only 4 per cent. being converted into non-volatile acids other than oxalic. The carbon balance on the Kohat kerogen shale resembles those on Kimeridge shale; although the rate of oxidation was much less and 7 per cent. of the carbon remained

unoxidized, the general distribution of carbon in the products was very similar.

TABLE IV.

Carbon Balances on Amherst and Kohat Kerogen Shales and Estonian Algal Limestone.

	Amherst.	Kohat.	Estonian.
Percentage carbon as :			
Carbonic anhydride	40·88	42·72	50·64
Acetic acid	2·92	3·98	8·05
Oxalic acid	27·24	31·48	28·55
Non-volatile, non-oxalic acids	3·99	14·60	3·82
Total C in products	75·03	92·78	91·06
Unoxidized carbon	25·08	7·07	8·69
Total	100·11	99·85 *	99·75
Distribution of Carbon in the Oxidation Products.			
Carbonic anhydride	54·5	46·1	55·6
Acetic acid	3·8	4·3	8·8
Oxalic acid	36·3	33·9	31·4
Non-volatile, non-oxalic acids	5·4	16·4	4·2
Total	100·0	100·0	100·0
Oxidation time, hrs.	132	125	115
Ratio $KMnO_4$/C	22·1	17·4	19·3

Scottish Kerogen Shales (Table V).—Three samples were examined, and also a sample of substantially ash-free (mineral matter 1·12 per cent.)

TABLE V.

Carbon Balances on Scottish Kerogen Shales.

	Broxburn Main.	Middle Dunnet.	Pumpherston.	
			Shale.	Kerogen.
Percentage carbon as :				
Carbonic anhydride	30·41	28·14	21·03	21·34
Acetic acid	3·57	5·09	4·46	3·81
Oxalic acid	11·67	14·92	10·68	9·64
Benzenoid acids	10·78	13·72	13·08	13·95
Total C in products	56·43	61·87	49·25	48·74
Unoxidized carbon	43·38	38·92	51·35	51·26 *
Total	99·81	100·79	100·60	100·00
Distribution of Carbon in Oxidation Products.				
Carbonic anhydride	53·9	45·5	42·7	43·8
Acetic acid	6·3	8·2	9·1	7·8
Oxalic acid	20·7	24·1	21·7	19·8
Benzenoid acids	19·1	22·2	26·5	28·6
Total	100·0	100·0	100·0	100·0
Time of oxidation, hrs.	190	120	125	75
Ratio $KMnO_4$/C	10·0	12·7	9·3	7·7

* Unoxidized carbon obtained by difference.

kerogen. The rates of oxidation were very low, and not more than 50–60 per cent. of the carbon was converted into soluble products. Considered together, the four carbon balances closely resemble one another, the most marked difference being the greater percentage of carbon dioxide from the Broxburn Main, which may be correlated with the much longer reaction time. Although the Pumpherston kerogen was attacked considerably more rapidly than the untreated shale, the two carbon balances show close agreement, indicating that the de-ashing process had little or no chemical effect on the kerogen. In view of the very long periods of oxidation and the almost negligible rate of reduction of permanganate in the later stages, it is probable that the non-volatile acids, other than oxalic, were almost entirely benzenoid, resembling those from bituminous coals. The percentage distribution of oxidized carbon in the Scottish shales is very similar to that obtained from a number of Irish peats as reported by W. A. Bone and others,[21] although with the peats the rate of oxidation was faster and complete oxidation was obtained.

Permanganate Bulk-Oxidations.—While the carbon-balance method of oxidation gives valuable information as to the quantitative distribution of the oxidized carbon between carbon dioxide, steam-volatile, oxalic, and non-volatile, non-oxalic acids, only very general conclusions as to the nature of the acids can be reached, and it is therefore necessary to carry out bulk oxidations to prepare the non-volatile and volatile acids in sufficiently large quantities to enable them to be separated and identified.

The quantity of material taken for a bulk oxidation depended on the percentage of kerogen in the sample and the yields of the acids to be obtained; this information was derived from the results of the carbon balance. The quantity required was generally from 500 to 1000 gms. The finely divided rock was suspended in about 10 litres of water, containing sufficient potassium hydroxide to give a ratio of alkali/kerogen of about 1·6; the liquid was gently boiled, and successive small quantities of solid permanganate were added to the solution, which was well stirred, the volume being maintained by the addition of boiling distilled water from time to time. When the rate of reduction of permanganate had fallen to about 1 gm. per hour, boiling was discontinued, the solution was filtered off, and the large quantities of oxides of manganese and residue from the shale were washed by boiling with distilled water. The combined filtrate and washings were evaporated to a known volume, usually 4 litres, and the distribution of carbon in the oxidized products was determined on a small fraction.

The bulk of the solution was acidified by the addition of the requisite quantity of concentrated hydrochloric acid, and the carbon dioxide was expelled by boiling under a reflux condenser. The acid liquor was next steam-distilled to separate the volatile acids, between 3 and 5 litres of distillate being collected; the acids were neutralized with sodium hydroxide and recovered as sodium salts by evaporating the solution to dryness. The oxalic acid was separated from the liquor in the distillation flask by precipitating it as calcium oxalate, thus giving a filtrate containing only non-volatile, non-oxalic acids and potassium chloride, from which the acids were obtained by evaporating to dryness and extracting successively with ether and acetone in a Soxhlet apparatus. By this means two mixtures

of crude acids were obtained, the compositions and equivalents of which could be determined.

The mixtures of crude acids were converted into their methyl esters by one or other of two methods. The ether-soluble acids were redissolved in ether and treated with diazomethane, formed *in situ* by the action of sodium hydroxide on nitrosomethyl urea, and after washing with sodium carbonate solution and distilled water the ether was distilled off, leaving a mixture of methyl esters. The acids which had been extracted with acetone were treated with ammonia of s.g. 0·88, maintained at 0° C., whereby benzene hexacarboxylic acid was separated as insoluble ammonium mellitate. The ammoniacal solution of the salts of the lower acids was boiled until neutral, and the acids were precipitated as their silver salts by adding a boiling solution of silver nitrate. The silver salts were filtered off immediately, washed, dried, and converted into the methyl esters by boiling under reflux with methyl iodide in dry ether. The insoluble ammonium mellitate was dissolved in water (above 0° C.), methylated in the same way, and the ester was recrystallized from absolute alcohol. Subsequent treatment of the methyl esters varied with each oxidation according to their quantity and character.

Four samples of kerogen rocks, Kimeridge, Broxburn Main, Ermelo, and Estonian, were investigated by bulk oxidation. Brief details are given below and the results are summarized in Table VI.

TABLE VI.

Acids Obtained by the Alkaline Permanganate Oxidation of Kimeridge, Estonian, Broxburn, and Ermelo Kerogen Rocks.

Kimeridge Kerogen Shale.	Estonian Algal Limestone.	Broxburn Main Kerogen Shale.	Ermelo Algal Shale.
CO_2.	CO_2.	CO_2.	CO_2.
Acetic acid.	Acetic acid.	Acetic acid.	Acetic acid.
Oxalic acid.	Oxalic acid.	Oxalic acid.	Oxalic acid.
Succinic acid.	—	—	—
Benzoic acid.	—	Benzoic acid.	—
o-Phthalic acid.	—	—	—
p-Phthalic acid.	—	—	—
—	—	Benzene pentacarboxylic acid.	Benzene pentacarboxylic acid.
Mellitic acid.	—	Mellitic acid.	Mellitic acid.

Kimeridge Kerogen Shale, Dorset.—1000 gms. of sample were oxidized in two equal portions, 3500 gms. permanganate being added to each over a period of 25 hours. The action was very vigorous, and got out of hand in the early stages unless external heating was discontinued. Altogether 50 gms. of crude non-volatile, non-oxalic acids were obtained, approximately half of which were soluble in ether, the remainder in acetone. Their composition was C = 40·2; H = 5·3; O = 54·5 per cent., which corresponds closely with that of succinic acid—namely, C = 40·67, H = 5·08, O = 54·25 per cent. The mixture of esters was a colourless, mobile liquid; on standing, no crystals separated, so the esters were fractionally distilled under a pressure of 1–4 mm. of mercury, six frac-

tions boiling between 35° and 140° C. being collected. The higher fractions were pale yellow, viscous liquids from which some methyl esters crystallized, whilst the lower fractions were colourless mobile liquids which could not be induced to crystallize. These fractions were hydrolyzed by boiling under reflux with 10 per cent. baryta, the solution was evaporated to dryness, the residue was acidified, and the acids were extracted with dry ether. Succinic acid preponderated in the lower fractions, and *o*-phthalic acid was also identified, whilst the methyl esters of *o*- and *p*-phthalic acids were identified in the higher fractions. From the acids extracted with acetone, the neutral methyl ester of benzene hexa-carboxylic acid (mellitic acid) was isolated.

A small quantity of white crystalline solid separated from the steam-distillate, the crystals being small plates, melting at 118° C. The only sparingly soluble acid which is volatile in steam is benzoic; the identity of the acid was confirmed by preparing the *p*-bromophenacyl ester, which melted at 119° C., thus proving benzoic acid. This observation acquires additional interest, since while the other acids recorded have been obtained from the oxidation of coal, *benzoic acid has never been found among the products*. After evaporating the neutralized steam distillate to dryness, the presence of acetic acid was confirmed by the formation of its *p*-toluidide (m.pt. 145° C.).

Estonian Algal Limestone.—300 gms. of a partly de-ashed sample were oxidized during 62 hours, 3455 gms. of potassium permanganate being reduced. Only acetic acid was identified in the steam-volatile acids, and no solid material separated from the distillate. The methyl esters of the non-volatile, non-oxalic acids were obtained as a pale yellow liquid; the quantity was too small for convenient fractionation, and since no crystalline material separated, the esters were hydrolyzed with baryta. Succinic acid was apparently present, but was not definitely identified, and no indications of other acids were obtained. Thus with the Estonian algal limestone the only oxidation products proved were carbon dioxide, acetic acid, and oxalic acid. No evidence of the presence of benzenoid acids was obtained.

Broxburn Main Kerogen Shale.—This was taken as being representative of the Scottish kerogen shales; 1000 gms. of the dry shale were oxidized with 2500 gms. of permanganate over a period of 70 hours. The carbon balance oxidations of these shales showed that a large proportion of the carbon remained unoxidized; determinations of the carbon remaining in the residue from the bulk oxidation showed that only 35 per cent. of the carbon had been converted into soluble products. The organic residue was investigated further by taking a representative sample, dissolving the oxides of manganese by means of sulphur dioxide, partly removing the mineral matter by acid de-ashing; the residue was then analysed. The composition found was C = 77·15, H = 9·20, O = 13·65, which showed that the residue was an intermediate product formed by the oxidation of the original kerogen, but which was still insoluble in aqueous alkali, and therefore not acidic. The low ratio of carbon to hydrogen (8·4) suggests a non-benzenoid character.

During the steam-distillation for removal of volatile acids a small quantity of benzoic acid, in the form of white crystalline plates melting

at 120° C., separated from the distillate, but the acidity of the distillate was due mainly to acetic acid.

The residual solution contained 54 gms. of oxalic acid, which was precipitated with the equivalent quantity of calcium acetate. By treating the acids with ammonia of s.g. 0·88 at 0° C., about 10 gms. of ammonium mellitate were obtained, part of which was converted into the neutral methyl ester (m.pt. 185° C.) via the silver salt. The remainder of the acids was taken up with ether and methylated, using diazomethane; on distilling off the solvent, a considerable portion of the esters crystallized at once. These crystalline esters were found to be largely the ester of benzene pentacarboxylic acid, forming small, pale yellow needles melting at 145° C., and a small amount of the ester of benzene hexacarboxylic acid. The quantity of liquid esters remaining was small, hence esters with low boiling points, such as methyl succinate and methyl phthalate, could have been present only in small quantities. Both the benzene pentacarboxylic and the benzene hexacarboxylic acid were present in considerable quantity, the former apparently preponderating, equivalent to about 5–10 per cent. of the kerogen.

Ermelo Algal Shale.—Study of the carbon balance oxidations of this shale showed that during the early stages of the reaction considerable proportions of non-volatile, non-oxalic acids were formed, which were subsequently further oxidized to carbon dioxide and oxalic acid. Hence, with a view to obtaining as high a percentage of these acids as possible, the bulk oxidation was carried out for only 15 hours; 500 gms. of dry shale were used, and the total quantity of permanganate reduced amounted to 2000 gms.

During the steam-distillation for separation of volatile acids, no benzoic acid crystallized, and only acetic acid could be detected in the distillate.

Analysis of a sample of the solution showed that 45 per cent. of the carbon had been oxidized to non-volatile acids, 10 per cent. being oxalic acid; this was removed as calcium oxalate and the remaining acids as ether- and acetone-extracts. The ether-soluble acids, approximately 40 gms., were redissolved and methylated with diazomethane. On removal of the ether, the esters deposited crystals, the mother-liquor was decanted off, the crystals were recrystallized from alcohol and the neutral esters of benzene pentacarboxylic acids identified. A considerable proportion of the esters remained as a colourless liquid, but no lower acids could be identified.

General Discussion and Conclusions.

Sedimentary deposits containing organic matter capable of yielding oil on distillation are widely distributed over the earth's surface, and are found in all geological formations, with the possible exception of the Pre-Cambrian. The majority were laid down in fresh or brackish water, although some occur in marine horizons. Microscopic examination shows that vegetable matter contributed largely as the source material of kerogen, some of the deposits (so far as the organic constituents are concerned) being made up almost exclusively of one particular plant material (such as algæ in the famous Torbanehill deposit, or spores in the Tasmanian spore-shale); the majority, on the other hand, exhibit an

almost irresolvable mass of macerated plant debris with but few spores and algæ.

Although the presence of numerous animal remains in some kerogen shales, such as the Kimeridge shale, has led several observers to postulate an animal origin for the organic matter, such evidence as is available is in favour of the view that, as in the coals, vegetable remains formed practically exclusively the parent material of the organic matter, and animal remains played little or no part. Thus, the kerogen shales of the Scottish Lothians, which occur in the Lower Carboniferous, were derived from plants similar to those which gave rise to the great bituminous coal-fields of Britain. Further, there is no reason to suppose that the proximate plant constituents of previous eras—namely, the cellulose, lignins, proteins, fats, waxes, and essential oils—differed in chemical constitution from those which form modern plants, although considerable variation in the relative proportions of those constituents may, doubtless, have occurred. There was therefore, as far as is known, little difference in the chemical characteristics of the parent materials of the members of the peat-to-anthracite series and of the kerogen rocks of different ages; their well-marked differences must have been in large measure due to the history of the deposits during and after their formation.

Excluding a few isolated and comparatively small deposits, such as those of Torbanehill and Joadja Creek, one very marked difference between kerogen rocks and coals is the much higher percentage of inorganic matter in the former. On removal of the organic matter by incineration, the mineral residue from coals falls to a fine powder, whereas that from the kerogen shales retains its original shape and size. The structural strength of the coals is therefore due to the highly compressed state of the organic material, whereas in the kerogen rocks the large content of inorganic matter provides the structural strength, and it may well be that the effect of pressure on the organic matter, in so far as this has contributed to the maturing of coals, may have been modified in the kerogen rocks.

The plant remains from which coals were formed was frequently accumulated *in situ*; kerogen rocks, on the other hand, are usually of drift origin, the vegetable debris being water-borne and deposited in shallow lakes and estuaries. During transportation, classification of the vegetable matter would take place, and, concomitantly, much of the less resistant constituents would probably be destroyed, leaving the more resistant materials to form the source material of the kerogen. On the other hand, in the formation of coals all the proximate constituents of the plants would be present.

As already pointed out, the determination of the empirical composition of kerogens presents certain difficulties, and only a limited number of results are available. Such data as there are indicate that kerogens have a higher content of hydrogen than members of the peat-to-anthracite series; the hydrogen in kerogen usually ranges from 8 to 12 per cent. as compared with from 2·5 to 7 per cent. in anthracite and peat, respectively. Some coals have abnormally high hydrogen, which, however, is still lower than the hydrogen in kerogen, and microscopic examination shows that these coals contain unusually large numbers of spores. Although spore cases have been detected in many kerogen rocks, their numbers

are usually small; they are certainly not present to any appreciable extent in Ermelo algal shale, Torbanehill, or Newnes algal rocks, the higher hydrogen contents of which may be due to the presence of algæ which are not found in bituminous coals. According to M. D. Zalessky,[22] the organic matter of the Balkash sapropelite (presumably botyrococcus) contains C = 73·76, H = 10·61, and O = 13·74. Further, Petrie [12] has reported that in a sample of Newnes algal shale from Joadja Creek, yielding only 6·55 per cent. of ash, the kerogen of which was estimated to consist of 90 per cent. of algæ, contained C = 79·75, H = 12·76, O = 5·81 per cent. These, however, are only isolated examples; in the majority of samples, including the Scottish, Kimeridge, Nevada, Kohat, Amherst, and St. Hilaire kerogen shales, very few algæ can be detected, the greater part of the organic matter being made up of tiny, partly carbonized fragments of plant remains and macerated vegetable debris. Furthermore, so typical an algal material as the Ermelo algal shale, the kerogen of which probably consists of some 50 per cent. of algæ, is decidedly low in hydrogen, the kerogen containing only 7·85 per cent. It seems therefore that either the algal material in this shale is associated with much debris which is low in hydrogen, or, alternatively, that the environmental conditions during and subsequent to deposition have resulted in a greater loss of hydrogen (probably as methane and/or water) than has occurred in shales such as that of Newnes. In this connection it may be mentioned that David White [23] suggested in 1925 that there were three separate "maturing" lines, one each for the humic coals, the cannels, and the alga bogheads, which merged into a common line in the semi-bituminous stage. In view of the paucity of evidence as to the true compositions of a sufficient number of kerogens, it would be premature to accept this suggestion; the available evidence appears to be adverse. What data there are suggest that, as in the peat-to-coal series, it is environment rather than original material which decides the characteristics of the final product.

In addition to carbon, hydrogen, and oxygen, nitrogen and sulphur are found in all kerogens, but how these elements are combined is at present unknown. There is also strong presumptive evidence that in some samples a small percentage of iron is combined in the organic matter.

Constitution.—A summary of the results of the alkaline permanganate oxidation of a number of kerogen rocks, together with data obtained from the oxidation of lignin and members of the peat-to-anthracite series (for comparison), is given in Table VII. It can be seen that, except for the Kimeridge shale, the kerogens were more resistant to oxidation than any of the coals other than the macroscopic constituent fusain. Practically complete oxidation (98–99 per cent.) of the coals was achieved in 50 hours, and even with anthracite, the most resistant type, 92 per cent. of the carbon had been converted into soluble products after 60 hours. In contrast to this, 43 per cent. of the carbon in Broxburn Main kerogen shale remained unoxidized after 190 hours. This failure to obtain anything like complete oxidation is partly due to the protective effect of the large proportion of mineral matter in most kerogen rocks, since carbon-balance oxidation on de-ashed samples showed that the rate of oxidation was nearly twice as fast. It should be noted that fusain showed great

TABLE VII.

Carbon-balance Oxidations.
Lignin, Peat-to-Anthracite Series [19] and Fusain.[24]

	Lignin.	Peats.	Brown Coals and Lignites.	Bituminous Coals.	Anthracite.	Fusain.
Percentage carbon as:						
Carbon dioxide	57–60	49–61	45–57	36–42	40	22
Oxalic acid	12–21	15–28	9–23	13–14	6	4·5
Acetic acid	2·5–6	2–5·5	3–7·5	1·5–4·5	2	0·5
Benzenoid acids	12–16	10–25	22–34	39–46	46	21
Unoxidized	—	—	—	—	8	52
Time required for oxidation, hrs.	Up to 50 or 60.					190

Kerogen Rocks.

	Kimeridge.	Kohat.	Estonian.	Amherst.	Ermelo.	Scottish.
Carbon dioxide	49	43	50	41	31	25
Oxalic acid	31	31	29	27	13	12
Acetic acid	8	4	8	3	5	4
Non-volatile, non-oxalic acids	11	15	4	4	17	3
Unoxidized	1	7	9	25	34	46
Time of oxidation, hrs.	56	125	115	132	145	125

resistance to oxidation, only about 50 per cent. of the carbon being attacked in 190 hours. There are, however, no other similarities between fusain and the kerogens; the distribution of carbon in the oxidation products is quite different, half the oxidized carbon from fusain appearing as benzenoid acids. Moreover, fusains are characterized by exceptionally low hydrogen contents as compared with the other macroscopic constituents of coals.

Considering the oxidations in detail, the Kimeridge kerogen was readily and completely oxidized; this ease of oxidation may perhaps be due to the high percentage of organic sulphur in the molecules. In the initial stages of the reaction some straight-chain acids are formed (succinic acid was isolated) which are subsequently further oxidized. Not more than 10 per cent. of the carbon is present as aromatic nuclei, the oxidation products including benzoic, *o*-phthalic, *p*-phthalic, and benzene hexacarboxylic acids, only the last being present in any quantity. The distribution of the carbon of the Kimeridge kerogen is similar to that of a number of Turraun peats examined at the Imperial College. There are, however, two important differences: (*a*) that a small quantity of benzoic acid was obtained from the kerogen, indicating the presence of simple aromatic nuclei, probably attached to side-chains, and (*b*) the greater part of the benzenoid acids consisted of benzene hexacarboxylic (mellitic)

acid, whereas in the oxidation products from peat, benzene pentacarboxylic acid preponderated over mellitic acid.

Carbon-balance oxidations of Ermelo shale indicated that, although a considerable proportion of straight-chain acids was formed by the initial oxidation, these acids were subsequently decomposed, but there still remained some 17 per cent. of the carbon as non-volatile, non-oxalic acids. In view of the time of reaction and the comparative readiness with which the aliphatic acids are oxidized to carbon dioxide and oxalic acid, it is probable that the remaining acids were almost entirely benzenoid. From the bulk-oxidation, considerable amounts of benzene penta- and hexa-carboxylic acids were isolated, and there was evidence of the presence of smaller quantities of less fully carboxylated benzenoid acids, although none were isolated. No benzoic acid was detected in the products of oxidation.

Whereas with the Kimeridge and Ermelo samples prolonged oxidation resulted in a decrease in the quantity of non-volatile acids other than oxalic, with Broxburn Main kerogen shale the reverse was observed. After an oxidation lasting 130 hours, 41 per cent. of the carbon was converted into soluble products, but only 0·5 per cent. was present as non-volatile, non-oxalic acids. On oxidizing a second sample for 190 hours, the percentage of these acids increased to 10·7 and the total carbon oxidized to 56·4 per cent. The carbon balances of the three Scottish samples show marked similarities; the distribution of the oxidized carbon among the products resembles that for brown coals and lignites, but large proportions of the Scottish kerogens remained unoxidized. Since it was possible to obtain almost complete oxidation of coals, it is suggested that certain kerogens contain one or more resistant constituents which are absent, or nearly so, from coals; microscopic examination suggests that the algæ may be the missing constituent, and subsequent experience on the oxidation of Newnes algal shale tends to confirm this suspicion. The oxidation products from Broxburn Main kerogen shale contained a considerable quantity of benzene hexacarboxylic acid, some pentacarboxylic acid and a trace of benzoic acid.

The oxidation of Estonian algal limestone was remarkable for the very small percentage of carbon oxidized to non-volatile acids other than oxalic; the identity of these acids could not be established; certainly, no ammonium mellitate could be separated by treating the crude acids with ammonia. Carbon balances indicated that a considerable quantity of non-volatile acids were formed in the earlier stages, but since these were further oxidized, they must have been succinic and other straight-chain acids. Only acetic acid was found in the steam distillate. These results are in agreement with the work published by P. N. Kogerman (*loc. cit.*), but the presence of mono- and di-basic fatty acids has not been confirmed.

No higher fatty acids than acetic were detected by Randall, Benger, and Groocock [20] in their examination of the oxidation products of more than fifty substances of known constitution, including hydrocarbons, aromatic hydrocarbons, aromatic substances containing a carbonyl group, aromatic carboxylic acids, heterocyclic compounds, ethers, and aldehydes. It should be noted that Kogerman's alkaline permanganate oxidation was

carried out at 30° C., whereas in the authors' experiments the solution was boiled.

While no detailed conclusions can yet be reached as to the chemical constitution of kerogen, the following inferences may legitimately be made:—

(i) The constitutions of some kerogens resemble, broadly, the constitution of coal in that there is definite evidence of a benzenoid structure, which is, however, less pronounced than that in coal. This may arise from a similarity in the original materials from which the kerogens were formed.

(ii) Other kerogens (notably that of the Estonian algal limestone) differ in constitution from coal, in that there is no evidence of benzenoid structure. This may be correlated with a difference in the original debris from which the kerogen was formed, or from different environmental conditions during and subsequent to deposition. In the inorganic matter of the Estonian material, calcium carbonate preponderates over clayey matter, which may have profoundly influenced that course of bacterial attack in the early stages of formation of kerogen; the effect of this limestone environment may also have modified the course of the changes which took place after the blanketing of the original deposit beneath subsequently-formed strata.

(iii) There is evidence that certain kerogens contain two types of compound, one comparatively easily oxidizable by alkaline potassium permanganate, the other highly resistant to attack. It is evident that in dealing with these kerogens, which include those of the Scottish, Ermelo, and Amherst kerogen rocks, stage oxidation will be necessary; preliminary oxidation with alkaline permanganate must be followed by more vigorous attack with a view to converting the "refractory" carbon into soluble products.

Finally, the authors desire to express their thanks to Professor A. C. G. Egerton, F.R.S., for helpful criticism and his continued interest in the work, also the Department of Scientific and Industrial Research for a grant to one of us (A. L. D.) which enabled the work to be carried out.

Imperial College,
18th July, 1940.

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THE COMPOSITION OF THE ASH OF TASMANIAN SPORE SHALE.

By G. W. Himus and S. Rudrakanchana.

In the course of the discussion on the paper by Down and Himus on the "Classification of Oil Shales and Cannel Coals" (*J. Inst. Petrol.*, 1940, **26**, 340), Mr. J. McConnell Saunders wrote, ". . . Tasmanite contains as kerogen, bodies which are supposed to be the preserved spores of lycopodium. Since the *Lycopodineæ* are quite remarkable for their high aluminium content, and since the spores are large and easily separated from the mineral matrix, the estimation of aluminium in their ash would appear to have more value than the analysis of the bulk material."

In their reply (p. 347) the authors agreed that ". . . it is fully realized that the nature of the inorganic matter and its relation to the kerogen require more detailed study . . .", and, in fact, this study is being carried on in a small way at the present time, and the suggestion of Mr. McConnell Saunders has been followed up with a view to ascertaining whether evidence of the lycopodian origin of the spores in Tasmanite could be substantiated by an examination of their ash.

To this end, a sample of Tasmanite was divided into fractions of different specific gravity by means of mixtures of bromoform, carbon tetrachloride, and benzene, with a view to concentrating the mineral matter in the sinks and the organic matter in the floats. By suitable treatment on these lines, concentrates yielding as little as 4·65 per cent and as much as 90·4 per cent of ash were obtained, together with a number of intermediate fractions, and the ashes left on incineration of several of these products were analysed. The results are tabulated below.

Compositions of the Ashes from Fractions of Tasmanian Spore Shale.

Ash, %.	4·65	83·36	88·30	90·4
	%	%	%	%
SiO_2 . . .	71·05	75·35	74·75	74·9
TiO_2 . . .	0·85	0·85	0·9	0·8
Fe_2O_3 and MnO .	6·45	5·4	5·8	5·95
Al_2O_3 . . .	11·7	12·1	12·05	11·85
CaO . . .	1·5	1·25	1·5	1·0
MgO . . .	2·55	1·75	1·8	1·65
SO_3 . . .	0·85	0·7	0·75	0·7

The results of the analysis of the ash from the de-ashed Tasmanite are probably somewhat (though not seriously) less accurate than the others, since the quantity of ash available was very small.

The table shows that the compositions of the ashes are surprisingly similar: whether the original material consisted largely of spores of nearly pure mineral matter made very little difference to the composition of the

ash. It is quite evident that there was no tendency to concentrate one element of the inorganic matter at the expense of any of the others during the process of de-ashing. The simple method suggested by McConnell Saunders of using the content of alumina as a criterion of the lycopodian nature of the spores in Tasmanite is therefore unsatisfactory. At the same time, it should be pointed out that the evidence provided by an examination of the products of the nitration of the spores (E. E. Kurth and L. J. Rogers. "Oil Shale and Cannel Coal," 1938, p. 201) that the spores may be derived from lycopods, is not called into question.

An interesting point which arose in the preparation of low-ash Tasmanite is referred to here because it may explain a difficulty which may be met with in de-ashing similar materials. It was found that better separation could be effected and a better yield of concentrated spores giving a lower ash could be obtained if the fine-grinding of the material were carried out by hand than if mechanical grinding were employed. When the sample was ground to *minus* 90-mesh (I.M.M.) in a steel end-runner mill, the yield of floats was lower and the ash on the floats at a given specific gravity was greater than if reduction had been carried out by hand. The explanation seems to be that sufficient heat was produced in mechanical grinding to cause incipient softening of the organic matter, which, coupled with the greater pressure in the end-runner mill, caused the finely-divided fragments of the spores to adhere to the fine particles of mineral matter, forming tiny compound particles which were sufficiently small to pass a 90-mesh screen. With the lower rate of grinding and the lower pressure obtaining when hand-grinding was practised, no such softening with consequent sticking together of organic and inorganic matter took place.

Imperial College.
12*th October*, 1941.

OBITUARY.

WILLIAM REGINALD ORMANDY.

W. R. ORMANDY was a Founder Member of the Institute of Petroleum, and served on the Council from 1919 to 1929. He was elected a Vice-President in 1926.

To those who had the honour of personal friendship the loss of Ormandy leaves a gap impossible to fill and a loss that is irreplaceable, for he was not only a man of science with many facets of interest, but also a very human and kindly personality. He was born in 1870, educated at Wigan Grammar School, and Owen's College, Manchester, where he graduated, becoming Bishop Berkeley Fellow in 1890. He took his Doctorate in 1894 after three years' work at Tubingen. For four years he taught at the Crewkerne Grammar School and at the Technical School, St. Helens. These five years probably helped to formalize Ormandy's mind—he always remained a teacher—informative in matter and impressive in diction, with a wide range of reading and knowledge and no little share of wisdom.

He had an astonishingly wide range of professional interests. He was research chemist to Messrs. Pilkington, Ltd., to the St. Helens Cable & Rubber Works, to Joseph Crosfield's of Warrington, and eventually head of a well-known firm of Consultants in Manchester and London.

Being a man who believed his fellow-creatures to be as interesting as chemical entities he rapidly found scope for his abundant energy in a multiplicity of societies. He served on the Council of the Institute of Petroleum for many years, on the Council of the Institution of Chemical Engineers, of the Institute of Metals and of the Ceramic Society. He was a Past-President of the Institute of Automobile Engineers, and Chairman of the Chemical Engineering Group of the Society of Chemical Industry.

He was specially interested in liquid and gaseous fuels, and perhaps it is not generally known that he was intimately concerned with the earliest work on hydrogenation of coal and oil carried out by Bergius. In point of fact he pioneered the development of this subject in Great Britain.

In no less degree was he active in insisting on the value of alcohol as a component of motor spirit, and in fact was Consultant to the Distiller's Company for many years.

One of his outstanding researches was concerned with the action of olefines on sulphuric acid. In this work he showed that a saturated hydrocarbon was produced. This statement brought about a storm of controversy, but subsequent investigation showed that Ormandy was right. Is it too much to say that here he was the lineal ancestor of modern processes of hydro-polymerization?

But reverting to Ormandy the man, those who knew him best carry pleasant memories of an outstanding personality, a controversialist brilliant in speech and repartee, kindly and tolerant in his dealings with his associates, a man of great knowledge but not deficient in understanding.

Ormandy was a particularly live and active member of our Institute until his health began to fail. He was a regular attendant at meetings and conferences, a ready speaker, and an excellent debater. He adorned every subject which he touched.

A. E. DUNSTAN.

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